COSMETIC CONTAINERS

Cross Reference to Related Applications

[0001] This application claims the benefit of US Provisional Patent application serial number 60/450,853 filed February 28, 2003.

Background of the Invention

[0002] This application relates to containers, and more particularly to containers for liquid cosmetics such as nail polish.

[0003] Nail products and other liquid cosmetics constitute an important segment of the cosmetic market. The world market for nail products in 2001 was estimated to be approximately $3 billion. These products make up approximately 11% of the world makeup market and approximately 13% of the U.S. makeup market. Europe is not far behind with nail products accounting for approximately 12% of this market. Japan, traditionally a skin care-led market, has less of a showing - with nail products accounting for approximately 7% of the country's $3 billion makeup market.

[0004] It has been said that nail polish is selected according to three factors: color, color and color. As a result, nail polish and similar liquid cosmetics have traditionally been packaged in clear glass bottles. Glass resists chemical attack by aggressive solvents in nail polish, and does not permit these solvents to permeate from the bottle during shipment and/or storage, which may cause undesirable changes in the composition of the product. Glass is substantially colorless, and provides consumers a substantially undistorted view of the color of nail polish within the bottle.

However, glass has some major drawbacks, principally container mass and limitation on container design. Thus, the cosmetic industry has sought to convert nail polish containers to plastic for weight savings and greater package design flexibility. BAREX®, a polyacrylonitrile copolymer of BP Chemicals Inc., has been used for nail polish containers. Unfortunately, BAREX® is inherently yellow, or may be deliberately tinted blue. In either case it distorts the packaged nail polish color.

Summary of the Invention

[0005] This invention provides novel bottles and other containers, and methods for producing these containers, with significant advantages for packaging nail polish, other liquid cosmetics and other materials so that the materials contained therein may be observed with less distortion. These containers are produced with substantially transparent cyclo-olefin copolymers, preferably norbornene-ethylene copolymers, blended with tint modifiers having a tint or hue that opposes the tint imparted to the container by the primary cyclo-olefin copolymer. Surprisingly, this produces a bottle with a significantly reduced tint, and displays nail polish, other liquid cosmetics and similar materials with less color distortion in a manner similar to conventional glass bottles. With the emphasis on color in the marketing and purchasing of these materials, this is a distinct and significant advantage.

[0006] Other advantages of this invention will be apparent from the following description.

Drawings

[0007] Figure 1 is a graph of the difference between Yellowness Index, for a glass nail polish bottle, and for bottles in accordance with this invention.

[0008] Figure 2 is a similar graph, but with data taken through a wall of the glass bottle, or a wall of bottles of this invention, that have been coated on the inside with a substantially colorless nail enamel.

[0009] Figure 3 is another graph of Yellowness Index data taken through the walls of samples that have been coated on the inside with white nail enamel.

DETAILED DESCRIPTION

[0010] Containers embodying this invention may be produced from various substantially transparent cyclo-olefin copolymers having a glass transition temperature (Tg) of at least about 80°C, preferably at least about 160°C. Cyclo-olefin copolymers with a Tg of at least about 160°C are especially preferred in applications where chemical resistance is paramount. However, cyclo-olefin copolymers with a Tg higher than about 80°C. can produce acceptable containers for many nail polish and similar liquid cosmetics applications, depending upon the desired chemical resistance and permeability of product ingredients. Cyclo-olefin containers with glass transition temperatures of at least about 100°C, at least about 120°C, at least about 140°C, at least about 160°C and at least about 180°C provide progressively higher chemical resistance, but become more brittle.

[0011] Cyclo-olefin copolymers have a lower density than glass, and offer design and fabrication flexibility typical of

to glass nail polish containers. Many cyclo-olefin copolymers are substantially transparent, and they do not have the safety and health issues associated with processing polyacrylonitrile. Unfortunately, products produced with these cyclo-olefin copolymers still tend to be slightly tinted, which reduces their usefulness for applications such as liquid cosmetic containers.

[0012] Surprisingly, we have found that the tint or discoloration perceived by a person viewing a product contained in bottles made from these copolymers can be reduced by adding a coloring agent or tint modifier to the cyclo-olefin copolymer. Both dyes and pigments impart color, however, during application of a dye, the dye loses its crystal structure at least temporarily, such as by dissolving or vaporizing. Pigments, on the other hand, retain their crystal or particulate form throughout the entire application process. As used herein the term "coloring agent" will be used to refer to the dye or pigment and the term "tint modifier" will be used to refer to the material added to the composition which imparts the color or tint to the container. Tint modifiers may be 100% coloring agents or they may be coloring agents mixed with other materials to dilute the coloring agent and make it easier to mix the coloring agent with the primary cyclo-olefin resin to make containers. Preferred tint modifiers comprise blends of the primary cyclo-olefin copolymer, or another cyclo-olefin copolymer, with one or more toners, dyes, pigments, color concentrates or other coloring agents. Tinted transparent toners are preferred because they do not detract from the transparency of the container.

[0013] The coloring agent should have a tint that opposes the tint imparted to the bottle by the primary cyclo-olefin

copolymer, and by the process for producing the product from this copolymer. Without being bound by this theory, it is believed that the tint of the coloring agent should be an "opponent" (as this term is used in the opponent process theory for viewing color) of the tint otherwise present in a comparable container without an additional coloring agent or tint modifier in accordance with this invention. Items molded from the cyclo-olefin copolymers preferred for this invention, described in detail below, typically have a light yellowish or straw-like tint or hue. For these materials, tint modifiers with a blue color are preferred. Tint modifiers with a red or green color may be acceptable in certain circumstances. If the bottle had a blue tint without the tint modifier, the tint modifier should be yellow. If the bottle had a red tint without the tint modifier, the tint modifier should be green. If the bottle had a green tint without the tint modifier, the tint modifier should be red.

[0014] Copolymers of norbornene (bicyclo[2.2.1]hept-2-ene) and ethylene, provided by Ticona GmbH under the trademark TOPAS®, are especially preferred for the articles and processes of this invention. These copolymers may be made by the processes disclosed in U.S. Patents 6,365,686 and 6,316,560 to Jacobs et al, assigned to Ticona GmbH, the disclosures of which are incorporated herein by reference. These patents disclose processes for producing highly transparent cyclo-olefin copolymers by polymerizing: 1) about 0.1 to 99.9% by weight, based on the total amount of monomers, of at least one polycyclic olefin; 2) from about 0 to 99.9% by weight, based on the total amount of monomers, of at least one monocyclic olefin; and 3) from about 0.1 to about 99.9% by weight, based on the total amount of monomers, of at least one acyclic 1-olefin in

the presence of a catalyst system. Polymerization is carried out with a metallocene catalyst, preferably a mixture of a metallocene and a co-catalyst such as an aluminoxane.

[0015] Preferred reactants for these processes, as disclosed in these patents, include norbornene and ethylene. With these materials, and the disclosed catalysts, highly transparent cyclo-olefin copolymers with high transparency and good mechanical properties can be tailored to many specific applications. Depending on package design, bottles and other containers may be made from these norbornene-ethylene copolymers with common techniques and equipment for making various plastic articles, such as injection blow molding, extrusion blow molding, injection molding and injection-stretch blow molding. Cyclo-olefins can be co-extruded with other substantially colorless, transparent polymers to produce composite containers with a cyclo-olefin inner or product contact layer and an outer layer of the other polymer.

[0016] These norbornene-ethylene copolymers, like many other cyclo-olefin copolymers, tend to have a slight yellowish tint or hue. Thus, tint modifiers with a blue tint are used to oppose the yellowish tint, reducing its intensity. Preferably, the tint is substantially eliminated, leaving a substantially clear bottle. Tint modifiers may be produced by blending, extruding and pelletizing a suitable resin, typically a cyclo-olefin copolymer with one or more coloring agents. The resin is preferably the same cyclo-olefin copolymer used as the primary copolymer for the container, or polymer with the same composition but with enhanced flow to promote dispersion. This reduces problems such as segregation in the extrusion process.

[0017] A variety of toners, dyes, pigments, color concentrates or other coloring agents, including but not limited to phthalocyanine or Cu phthalocyanine pigments and anthraquinone dyes may be used to produce the tint modifier. The optimal amount or level of coloring agent for any given tint modifier or final article will depend upon a variety of factors, such as the intensity of the coloring agent and the intensity of the tint imparted to the bottle by the primary cyclo-olefin copolymer. Suitable levels may be determined by those skilled in the art by experimentation.

[0018] The primary cyclo-olefin copolymer and the tint modifier may be obtained from suppliers in pelletized form. Preferably the pellets of the cyclo-olefin copolymer and pellets of the tint modifier are approximately the same size to facilitate blending and extrusion. Typically the size of the pellets may be about 1/16 inch in diameter and about 1/8 inch long. They may be mixed in a blender or other conventional equipment with other materials conventionally used in thermoplastic molding processes, such as waxes, antistatic agents and other process aids. The blend is transferred to an extruder, which melts the resins, producing a substantially homogeneous mixture, and forces the mixture into molds in the desired size and shape.

[0019] Figures 1, 2 and 3 illustrate the beneficial results obtained with this invention. These figures chart the Yellowness Index, for samples of norbornene-ethylene ("COC") bottles with varying levels of tint modifier, in comparison with a typical glass nail polish bottle. Figures for bottles produced with natural BAREX® and blue tinted BAREX® polyacrylonitrile ("PAN") are also included. Figure 1

illustrates the change in Yellowness Index for uncoated bottles of this invention versus an uncoated glass sample. Figure 2 illustrates the change in Yellowness Index versus glass, with the materials coated with a colorless nail polish enamel, viewed through the norbornene-ethylene sample or the glass sample. Figure 3 illustrates the change in Yellowness Index for samples of the norbornene-ethylene containers or the glass container with the samples coated with white, substantially opaque nail polish enamel. The data for the graphs in Figures 1 and 2 was obtained with light transmitted through the samples. The data from Figure 3 was obtained with light transmitted through the samples onto the inner surface of the white enamel coatings, and reflected back through the walls of the samples.

[0020] As may be seen from Figures 1-3, the tint of cosmetic containers produced with norbornene-ethylene containers and a suitable toning agent may be varied in accordance with this invention to give the containers a Yellowness Index that varies from the Yellowness Index for a typical glass nail polish container by about -0.4 to +0.5 depending on the amount of tint modifier or concentrate added to the primary norbornene-ethylene copolymer, and about -2.5 to about +0.5 for reflected radiation (Figure 3). For the containers and processes of this invention, we prefer to use an amount of tint modifier sufficient to give the finished bottles or the containers a comparative transmitted Yellowness Index, as compared with a typical clear glass nail polish bottles, of about ±0.2, as determined by ASTM D1925-70 (reapproved 1988) Standard Test Method for Yellowness Index of Plastics. This Standard was withdrawn by ASTM in 1995 but is still frequently used by manufacturers to evaluate plastic materials and products. Advantageously, finished containers

according to the present invention will have a comparative Yellowness Index, i.e. a Yellowness Index relative to the Yellowness Index for a typical clear glass nail polish bottle, less than or equal to about +0.2. Containers with a comparative Yellowness Index between about zero (0) and about +0.1 are especially preferred. As may be seen from Figures 1 and 2, the glass used in these tests had a Yellowness Index of 0.31. Through the use of this invention, this tint can be substantially, if not completely, eliminated, leaving the consumer with an undistorted view of nail polish or other materials within the container.

Example 1

[0021] Sample bottles were produced by injection blow molding a norbornene-ethylene copolymer supplied by Ticona GmbH as TOPAS® 8007 resin, having a norbornene/ethylene ratio of about 36/64 and a glass transition temperature (T_g) of about 80°C. These bottles were exposed to Avon nail polish in accordance with ASTM test method D2684. The bottles softened and split in less than five days at 120°F. These materials were not considered suitable for the most demanding nail polish applications. However, they may be suitable for less aggressive nail polish or other cosmetics.

Example 2

[0022] Sample bottles were produced by injection blow molding a norbornene-ethylene copolymer supplied by Ticona GmbH as TOPAS® 6105 resin, having a norbornene/ethylene ratio of about 57/43 and a glass transition temperature (T_g) of about 160°C. These bottles were exposed to Avon nail polish in accordance with ASTM

test method D2684. These materials were considered suitable for many nail polish and other liquid cosmetic applications.

Example 3

[0023] Batches of the norbornene-ethylene copolymer described in Example 2 were blended with varying quantities of a transparent blue tint modifier supplied by Clariant International Ltd. as Clariant OM51620027. Samples were prepared to demonstrate the effect of this invention on the tint of a cyclo-olefin copolymer bottle. Each batch contained 10 pounds of TOPAS® 6015 D-62 copolymer containing about 57% norbornene and about 43% ethylene, an amount of the Clariant OM51620027 tint modifier calculated to produce the levels of tint modifier in Table 1 below (for example, the sample listed as having 0.5% tint modifier received 22.7 grams of the Clariant OM51620027 tint modifier) and conventional processing aides. Each batch was blended and supplied to an extruder which melted the resins and extruded the molten and homogenized material to a series of perform molds to produce bottles approximately 1.86 in. in diameter and 3.8 in. high, with a wall thickness of about 45 mils. After steady state conditions were achieved, approximately 25 bottles were produced from each batch and samples were cut from these bottles for transmission/reflectance testing. BAREX® 210I natural resin and BAREX® 210I blue tint polyacrylonitrile resin, currently available from BP Amoco were processed in a similar manner to produce samples for comparison. Base line samples were obtained from glass bottles having a composition of SiO_2-72%, Al_2O_3-2%, Na_2O-13.5%, K_2O-0.1%, CaO-9.5%, MgO-1.5%, Fe_2O_3-0.02% and SO_3-0.2%, a conventional material for glass nail polish bottles. The glass samples had a wall

thickness approximately equal to the thickness of the norbornene-ethylene and BAREX® samples.

[0024] Yellowness Indices for these materials were determined in accordance with ASTM Standard Test Method for Yellowness Index of Plastics D1925-70 (reapproved 1988), commonly used for determining the degree of yellowness (or change of degree of yellowness) under daylight illumination of homogeneous, non-fluorescent, nearly colorless transparent or nearly white translucent or opaque plastics. As used herein, the terms "Yellowness Index" and "YI" should be understood to mean Yellowness Index as defined in the ASTM Standard Test Method, i.e., the magnitude of yellowness relative to magnesium oxide for CIE (Cucian Internationale Del'eclairage or International Commission on Illumination, Vienna, Austria) Source C. Yellowness Index is expressed as follows:

$$YI = [100(1.28X_{CIE} - 1.06Z_{CIE})]/Y_{CIE}$$

where: X_{CIE}, Y_{CIE}, and Z_{CIE} are tristimulus values of the specimen relative to Source C.

[0025] A positive Yellowness Index describes the presence and magnitude of yellowness. A specimen with a negative Yellowness Index will appear bluish.

[0026] These tests were conducted in a MacBeth Spectralight light booth Model SP7-75B, employed to control parameters influencing appearance such as background color, light source and the like. The specimens were illuminated with a Daylight D75 light source. Transmission and reflectance values were obtained with a Daylight D65 light source. Values for Yellowness Index were obtained with a Datacolor International Model SpectraFlash SF600 PLUS-CT spectrophotometer

using ColorTools/Version 2.2 software. This data is set forth in Table I.

Table I

Differences in Yellowness Index vs. Percentage of Tint Modifier

Transmission Uncoated Samples		**Transmission Coated Samples Clear Enamel**		**Reflectance Coated Samples Opaque Enamel**	
% Tint Modifier	Delta YI vs Glass	% Tint Modifier	Delta YI vs Glass	% Tint Modifier	Delta YI vs Glass
0	0.48	0	0.52	0	0.53
0.1	0.36	0.1	0.37	0.1	0.18
0.25	0.27	0.25	0.29	0.25	0.14
0.5	0.21	0.5	0.28	0.5	0.4
0.75	0.23	0.75	0.22	0.75	-0.25
1	0.17	1	0.19	1	-0.26
1.25	0.13	1.25	0.09	1.25	-0.62
1.5	0.11	1.5	0.13	1.5	-0.21
1.75	0.05	1.75	0.04	1.75	-0.77
2	-0.08	2	-0.09	2	-1.34
2.5	-0.13	2.5	-0.15	2.5	-1.62
4	-0.45	4	-0.45	4	-2.61
YI glass = 0.31		YI Glass + Colorless Enamel = 0.38		YI Glass + White Enamel - 3.01	
YI Barex 210I Natural = 9.57		YI Barex 210I Natural + Colorless Enamel = 9.55		YI Barex 210I Natural + White YI Enamel = 17.76	
YI Barex 2101 Blue Toned - 3.40		YI Barex 210I Blue Toned + Colorless Enamel = 3.42		YI Barex 210I Blue Toned + White Enamel = 0.50	

[0027] Of course, while the invention has been described in detail, with particular emphasis on preferred embodiments, those skilled in the art should also appreciate that many variations

and modifications to and variations of the embodiments described herein within the spirit and scope of this invention, which is defined by the following claims.